A new transient measuring method of the thermal diffusivity of molten salts is presented. To improve the accuracies of the temperature measuring locations and to remove the thermal effects of the container, the liquid sample is held in thin layers between a few parallel copper plates by its own surface tension, and the thermal diffusivity is determined from the temperature responses of the copper plates for arbitrary heating, using the computer simulation. The measured results for NaNO₃ and LiNO₃ are compared with the results by other researchers, and the accuracy of the results is discussed considering the effects of the error factors included.

Key Words: Thermal Engineering, Thermophysical Properties, Thermal Diffusivity, Transient Absolute Measurement, Molten Salt, Lithium Nitrate, Sodium Nitrate

1. Introduction

It is important to know the thermal properties of molten salts systematically in designing a latent heat thermal energy storage apparatus for such as solar generation plants, using the molten salts as the high temperature use PCM (phase change material). Under the present situation, however, the reliable measured data are not sufficient, and even the measuring method for the molten salts is not established yet. In this paper, a transient measuring method of the thermal diffusivities of molten salts in high temperature region is proposed. Concerning the previous measuring methods of thermal properties of molten salts, Hoshi and Nagashima✓ showed a method using a liquid metal probe as the line heat source. Kato et al.✓✓ proposed a method utilizing a ceramic container, and Araki✓✓✓ showed a method enclosing the PCM in a thin disk metal container. Some of the authors✓✓ also proposed a method, where the thermal conductivity and the specific heat over a wide temperature range are determined by a single continuous heating. In the measurement of the thermal properties of the molten salts, including this method, the difficulty arises not only from the high temperature, but also from their corrosiveness and electrical conductivity.

In the method described here, the required boundary conditions are easily realized, although the pulswise or stepwise heating boundary conditions are generally given in most of the previous methods mentioned above. In this method, the surface of a semi-infinite liquid sample material is heated by an arbitrary time function, and the thermal diffusivity of the sample is determined from the temperature response at a certain point within the sample by numerical calculation. In such an arbitrary heating measuring method for nonconductive materials, the accuracy of the temperature measuring point location within the sample, which depends on the dimensions of the temperature measuring sensor, is very important, because the temperature gradient in the sample is high✓✓✓. In the method proposed here, conductive metal plates, having known thermal properties, are inserted in the sample, and the plate temperatures are measured to solve the above problem of the measuring location accuracy. Moreover, to remove the heat loss through the container walls, which is peculiar to the thermal property measurement of the liquid, the periphery of the liquid sample material of this method is suspended by its own surface tension, applying the method which was first used by Tada et al.✓✓✓ in the laser flash method.

Apart from this work, Okada and one of the authors✓✓✓ reported a method, where the thermal properties were determined from the temperature response within the sample by numerical calculation, although the temperature measuring sensor was directly set in the sample. In the method, however, the sample material was limited.
to the solid, and the sample was heated symmetrically. Therefore, it is difficult to use the method for the thermal property measurement of the liquid materials such as molten salts.

Nomenclature

\( a \): thermal diffusivity, \( m^2/s \)

\( \Delta a \): error in thermal diffusivity, \( m^2/s \)

\( \delta T \): modification in thermal diffusivity (Ref. Fig.2), \( m^2/s \)

\( E_i \): Biot number = \( W_i/k_i \)

\( c \): specific heat, \( J/(kg\cdot K) \)

\( k \): thermal conductivity, \( W/(m\cdot K) \)

\( L \): thickness of each layer (Ref. Fig.1), \( m \)

\( i \): location of the back surface of each layer (Ref. Fig.1), \( n \)

\( m \): the maximum depression of the meniscus, \( m \)

\( t \): time, \( s \)

\( W \): equivalent heat transfer coefficient, \( W/(m^2\cdot K) \)

\( x \): ordinate (Ref. Fig.1), \( m \)

\( X \): factor causing the error

\( \theta_i \): the \( i \)-th layer temperature variation from the initial temperature, \( K \)

\( \Delta \theta_i \): the maximum deviation of the initial temperature (Ref. Fig.12), \( K \)

\( \theta_{z1} \): temperature deviation of the metal second layer (at \( x=0 \)) from the initial temperature, \( K \)

\( \theta_{z2} \): temperature deviation of the metal fourth layer (at \( x=L \)) from the initial temperature, \( K \)

\( \rho \): density, \( kg/m^3 \)

Subscripts and superscripts

\( 1 \): sample material

\( 2 \): metal plate

\( i \): the \( i \)-th layer (\( i=0 \sim 4 \))

\( * \): the real value

\( \circ \): calculated value

2. Principle of Measurement

As shown in Fig.1, the sample material layers (the first, the third and the fifth sample layers) and the metal plates (the second and the fourth copper layers) having known thermal properties are piled alternately, and are heated uniformly from the first layer surface with an arbitrary function of time. When the temperature variation by heating is small and the thermal properties are assumed to be constant, the basic equation, the initial conditions and the boundary conditions become as follows.

Basic equation:

\[
\frac{\partial \theta_i}{\partial t} = a \frac{\partial^2 \theta_i}{\partial x^2} \quad (i=1 \sim 4) \quad (1)
\]

Initial conditions:

\[
t = 0, \quad \theta_i = \theta_i(t) \quad (i=1 \sim 4) \quad (2)
\]

Boundary conditions:

\[
x = 0, \quad \theta_i = \theta_i(t) \quad (3)
\]

\[
x = L, \quad \theta_i = \theta_i(t)
\]

In the above equations, \( \theta_i(t) \) denote the temperature variations at \( x = 0 \) and \( x = L \), respectively.

When the dimensions of each layer, \( L_i \) (\( i=1, 2, 3, 4 \)), the thermal properties of the metal plates (thermal conductivity, \( k_i \), specific heat, \( c_i \), and density, \( \rho_i \)), the specific heat, \( c_i \), of the sample and the density, \( \rho_i \), of the sample are given, the time dependency of the temperature variation, \( \theta_i(t) \), at \( x = L \) (the center of the second layer) under an arbitrary heating of the system is determined only by the thermal diffusivity of the sample, \( a_1 \), and by the time dependencies of the temperature variations, \( \theta_i, \theta_i \) at \( x = 0 \) (the heating surface) and \( x = L \). Therefore, if the time dependencies of the temperature variations, \( \theta_i, \theta_i \), are measured at the same time, a unique thermal diffusivity, \( a_1 \), fitting the dependencies, should exist.

A flow-chart to determine \( a_1 \) from \( \theta_i, \theta_i \) and \( \theta_i \) by numerical calculation is shown in Fig.2. First of all, the measured time dependencies of the temperature variations at the heating surface and the fourth layer copper plate (\( \theta_i, \theta_i \)), the heat capacity of the sample material, the thicknesses of the layers and the thermal properties of the metal plates are input. Next, the thermal diffusivity, \( a_1 \), is assumed and the calculated time dependency at the second layer temperature variation, \( \theta_i \), based on the assumed thermal diffusivity, is compared with the measured second layer temperature variation, \( \theta_i \). If the calculated and measured temperature variations do not agree within 0.5%, the thermal diffusivity is set at a modified value and the above process is repeated. By this method, many results for thermal diffusivity, \( a_1 \), corresponding to each measuring time, are obtained simultaneously by a single measurement, although they are almost the same. Because the finite difference method is used in
the process of calculating \( \Theta \), the complicated real measuring conditions, which cannot be considered in the analytical solution, can also be included in the numerical calculation process.

Next, the effects of inserting metal plates at temperature measuring points within the sample material are explained below. Figure 3 shows the calculated temperature distribution after 60 seconds under a stepwise heating, where sodium nitrate and copper are used as the sample material and the inserted plates, respectively, and the heat flux at \( x = 0 \) is 11.63 kW/m². In Fig.3, the solid line (A) denotes the case without the copper plates, and the dotted line (B) denotes the case where a copper plate of thickness 1 mm is inserted at the location \( x = 2.8 \)~\( 3.0 \) mm. If the temperature at \( x = 2.5 \) mm is measured by a sufficiently thin sheath thermocouple of diameter 0.5 mm in the case of Fig.3A, where the copper plate is not used, the uncertainty of the thermocouple location is about 20%, although the center location of the thermocouple is carefully determined. Then, the accuracy of the temperature measurement is very low, because the curve A has a considerably steep gradient. On the other hand, in the case of line B in Fig.3, where a copper plate is inserted, the temperature within the copper plate is almost uniform, because the thermal conductivity of the copper is much higher than that of sodium nitrate. And the accurate temperature measurement is possible, only if the thermocouple is set within the copper plate without a contact resistance and the plate location is accurately determined.

3. Measuring Apparatus and the Measuring Method

3.1 Measuring apparatus

The measuring section is shown in Fig.4. The heater and two copper plates with thicknesses 2, 1.5 mm and with diameter 40 mm are piled up with spacers interposed between them to determine the plate locations accurately, and are fixed. Then, the liquid sample is poured to fill the gaps between the plates. Between the lower copper plate and the bottom base plate, two sample layers are provided to

![Fig.2 A flow chart to decide the thermal diffusivity, \( \alpha \). (\( \Theta_0 \) and \( \Theta \) denote the temperatures at the second layer center by measurement and by calculation, respectively.)](image)

![Fig.3 The change in temperature distribution by inserting a metal plate](image)

![Fig.4 The measuring apparatus](image)

![Fig.5 Details of the heater section](image)
get the initial condition easily. The details of the heater section are shown in Fig.5. A sheath heater with diameter 1 mm densely wound in a solution is placed between copper plates with thickness 3 mm, and fixed by solder, so that the heat flux becomes uniform and the heater is insulated electrically from the molten salt. The spacers are pieces of a crystallized glass with diameter 1.0 mm and thickness 1.635 mm or with diameter 2.0 mm and thickness 2.380 mm, considering the thermostability, the corrosion resistance, the thermal expansion and the thermal conductivity. The spacers are placed at three points near the periphery of the copper plate. The crystallized glass withstand a temperature of about 1000°C. The thermal conductivity and the coefficient of thermal expansion are 1.67 W/(m·K) and 9.4×10⁻⁴ K⁻¹, respectively. As shown in Fig.6, the heater plate and the second layer copper plate have three holes with diameter 0.8 mm, drilled parallel to the plane surfaces from the sides. The ends of the holes are located at the disk center and at the points 8 and 15 mm from the center, respectively. The C-A sheath thermocouples with diameter 0.5 mm are set in the holes and the gaps are filled with solder. In the same way, a C-A sheath thermocouple is also set at the disk center of the fourth copper plate. Because the temperature distribution within a high conductive metal plate is nearly uniform, as mentioned in chapter 2, the measured temperatures by the sheath thermocouples of Figs.5 and 6, which are attached to the heater plate and the fourth layer metal plate, are used as \( \theta_6 \) and \( \theta_5 \).

The sample material and the whole measuring section, shown in Fig.4, are kept in the double copper containers shown in Figs.7(a)(b). Containers are used to make the ambient temperature around the measuring section uniform and to supply the sample material smoothly to the measuring section, as explained later. The containers of Fig.7 and the measuring section of Fig.4 are nickelplated, considering the corrosion.

The containers of Fig.7 are again placed in an electrical furnace, shown in Fig.8. The temperature distribution within the furnace is controlled by a side main heater and by an upper subheater. Fireproof bricks wrapped with aluminum foil are used for upper and lower insulations.

3.2 Method to pour the sample material

The surface tension of the molten salt is comparatively high being generally 1.5 times that of the room temperature water. In this method, therefore, the sample material is held between the copper plates by its own surface tension, as shown in Fig.4. Then, the one-dimensional heat flux is easily realized, and the apparatus becomes compact. Moreover, the initial temperature condition is easily obtained.

As shown in Fig.7(b), the sample material and the measuring section are initially set together in the container. Then, a copper ring is slowly sunk between the measuring section and the container wall to raise the liquid surface, as shown in Fig.8. The layout of the apparatus.
in Fig.7(a). When the upper surface of the first layer sinks under the liquid surface, the container is carefully swung to remove the bubbles from the measuring section. Thereafter, the ring is again pulled up slowly, as shown in Fig.7(b), and the sample material remains in the first, third, fifth, and seventh layers, although the liquid surface goes down.

The thicknesses of the first and third layers, which contain the sample and affect the accuracy of the measurement, are about 1.6 mm and 2.4 mm, respectively.

3.3 Measuring procedure

The measuring procedure is as follows:

(1) The sample material fills the measuring section by the method of 3.2. Then, the apparatus is quickly pulled out to get a photograph of the meniscus. At the same time, the sample layers are checked to see there are no bubbles within them.

(2) The container, the copper plates, and the sample are kept at a uniform temperature.

(3) The heater is operated properly, and the temperature variations of the heater and two copper plates are measured and recorded every 1 s for 30 s.

(4) After the measurement, the meniscus is again photographed in the same way as in the above (1) to confirm that the shape remains unchanged through the measurement.

(5) The thermal diffusivity is determined according to the method of chapter 2.

4. Results of Measurement

To examine the accuracy of this measuring method, the thermal diffusivity of pure water, which was known accurately, was measured in the temperature range 20~25°C. The results agreed with the values shown in Ref.(10) within an accuracy of 2%.

Next, lithium nitrate (LiNO₃; melting point 294°C) of high purity was measured in the temperature range 300~380°C. The results are shown in Fig.9. In Fig.9, the symbols □ denote the maximum variable range of the measured results, which were determined at successive measuring times through a single measurement. It is found that the variation averages ±2.3%. The maximum temperature rise at the heater surface was about 7°C. The size of the meniscus was measured and the effects were modified by the method which was confirmed to be effective with distilled water. In the measured results of Fig.9, the modifications were based on the mean size of the meniscus determined from photographs. By the way, the scatter of the meniscus sizes is comparatively small, and its effects on the measured thermal diffusivity are approximately ±1.5%. The measured results by the other method are also shown in Fig.9 for comparison. The results by this method are included within the range by other authors.

The measured results for the thermal diffusivity of sodium nitrate (NaNO₃) are shown in Fig.10, compared with the results by other authors. A very pure sample, dried for long time in vacuum, was used. The results for the sample which was not dried in vacuum are also shown with symbol ◆ for reference. The results of this method agree fairly well with the results by other methods. In the measurement of Fig.10, the sample layer thicknesses were slightly greater (the first layer: 2.0 mm, the third layer: 3.0 mm).

5. Discussion on the Error of Measurement

The thermal diffusivities of sodium nitrate measured by other authors are scattered over a wide range, 1.5~2.0×10⁻⁷ m²/s, as shown in Fig.9. Although the deviation among the data by a single method is comparatively small, it is probable that the data may include the error particular to each method. Then, the maximum error of this method was estimated by numerical simulations concerning the results with sodium nitrate.

The errors particular to the method arise from slight discrepancies among the assumed conditions in the measuring principle, the actual apparatus and the actual measuring process. The important error factors in this method are listed in
the left column of Table 1. For example, the error relating to the first layer sample thickness, \( L_1 \), shown in the first column of Table 1, will be discussed below. If the layer thickness, \( L_1 \), is kept at a constant through the measurement and the exact value of \( L_1 \) is used in the calculation process of Fig.2, there is no problem. But, in an actual case, there happens a small difference, \( \Delta L_1 \), between the real value, \( L_1 \), and the value used in the calculation of Fig.2, due to the thermal expansion or a small error in the spacer height measurement. Then, the determined thermal diffusivity, \( \alpha_1 \), from Fig.2 necessarily includes the error, \( \Delta \alpha_1 \). The relation between \( \Delta L_1 \) and \( \Delta \alpha_1 \) is discussed below. And the error, \( \Delta \alpha_1 \), due to the uncertainty in \( L_1 \) is shown, estimating the value of \( \Delta L_1 \). These discussion processes were done concerning all the error factors given in Table 1.

The simulation process and the method to estimate the error of the measured thermal diffusivity, caused by each factor in Table 1, are shown in Fig.11. In Fig.11, \( X \) denotes the error factor, being checked, and \( X^* \), \( \alpha \), \( \alpha^* \), of the two copper plates are calculated by the finite difference method, using the real thermal diffusivity, \( \alpha \), the real value of the factor, \( X^* \), and the real values of the other specifications. Next, it is assumed that \( X \) includes the error, \( \Delta X \). The thermal diffusivity is determined in the process of Fig.2, using \( (X^* + \Delta X) \) and real temperature responses calculated above. The thermal diffusivity, thus determined, includes the error, \( \Delta \alpha \). That is, the relation between \( \Delta X \) and \( \Delta \alpha \) is obtained. In the same way, such relations are calculated for all error factors.

Table 1 Errors by various factors

<table>
<thead>
<tr>
<th>error factors</th>
<th>( X - X^* ) or ( X^* )</th>
<th>( \Delta \alpha_1 )</th>
<th>actual error range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1st layer thickness ( L_1 )</td>
<td>5%</td>
<td>1.9%</td>
<td>7.9%</td>
</tr>
<tr>
<td>2. 2nd layer thickness ( L_2 )</td>
<td>5%</td>
<td>2.0%</td>
<td>2.5%</td>
</tr>
<tr>
<td>3. 3rd layer thickness ( L_3 )</td>
<td>5%</td>
<td>2.0%</td>
<td>2.5%</td>
</tr>
<tr>
<td>4. Sample heat capacity ( c_p )</td>
<td>10%</td>
<td>5.0%</td>
<td>5.0%</td>
</tr>
<tr>
<td>5. Copper heat capacity ( c_p )</td>
<td>5%</td>
<td>1.0%</td>
<td>1.0%</td>
</tr>
<tr>
<td>6. Copper thermal conductivity ( k_\text{Cu} )</td>
<td>11%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>7. Init. temp. dist. ( \Delta \theta (\degree C) )</td>
<td>2.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>8. Heat loss from side wall ( Q_\text{side} )</td>
<td>0.1%</td>
<td>0.5%</td>
<td>0.5%</td>
</tr>
<tr>
<td>9. Meniscus ( h (\text{mm}) )</td>
<td>0.5%</td>
<td>0.2%</td>
<td>0.2%</td>
</tr>
<tr>
<td>10. Flatness ( \Delta L/L )</td>
<td>5.3%</td>
<td>3.0%</td>
<td>3.0%</td>
</tr>
</tbody>
</table>

The relations are shown in the second and the third column of Table 1. Although it is impossible to use the real values in the above discussion, representative measured results or the values in the reference papers may be used for the purpose of error estimation. In the second column of the table, the values \( (X - X^*)/X^* \) are given for items 1 - 6 and 10, and the values \( (X - X^*) \) are given for items 7 - 9. The assumed real values of dimensions and thermal properties in the simulation are shown below:

\[
L_1 = 1.600 \text{ mm}, \quad L_2 = 2.000 \text{ mm}, \quad L_3 = 2.400 \text{ mm}
\]

\[
c_\text{p1} = 2.512 \times 10^5 \text{ J/(m}^2\text{·K)}, \quad c_\text{p2} = 3.714 \times 10^5 \text{ J/(m}^2\text{·K)}
\]

\[
k_\text{Cu} = 0.465 \text{ W/(m·K)}, \quad k_\text{Si} = 365.4 \text{ W/(m·K)}
\]

Next, the error factors 7 - 10 of Table 1 are briefly explained below.

Initial temperature distribution: Although the initial temperature distribution within the sample is assumed uniform \( (X = \Delta \theta = 0) \) in the calculation of Fig.2, a slight temperature distribution may occur in an actual case and may cause an error in the measured thermal diffusivity. The error was estimated for the case where a constant gradient initial temperature distribution existed in a direction perpendicular to the sample layer, as shown in Fig.12, and the temperature difference between the heater and the fourth plate was \( X^* = \Delta \theta ^\circ \text{C} \).

Heat loss from the side wall: Although the side wall is assumed adiabatic \( (X = W/L, \Delta \theta = 0) \) in the calculation of Fig.2, a small amount of heat loss due to the outside environment may cause an error. The real value of the other items

\[
\text{Real value} \quad X^*, \alpha^* \quad \text{Simulation by the FDM}
\]

Calculation of expected variations of \( \alpha_1 \) and \( \alpha_4 \) for \( X^* \) and \( \alpha^* \)

Decision of \( \Delta \alpha_1 \) affected by \( \Delta X \), using Fig.2

\[
a_1 = a_1^* + \Delta a_1
\]

Fig.11 A flow chart for error analysis

Fig.12 The initial temperature distribution
to natural convection or radiation in an actual case may cause an error in the measured thermal diffusivity. The error was estimated for the case where the heat losses by natural convection and radiation occurred, as shown in Fig. 13 (X' = W/L, A/k. 4). The symbol W denotes the equivalent heat transfer coefficient including the radiation. The value of W was assumed the same for all layers. The side wall was assumed black to estimate the maximum error.

Meniscus: Although the sample outer radius is assumed the same as that of the copper plate in the calculation of Fig. 2, the actual sample radius is slightly smaller than the plate radius, as shown in Fig.14, and a contraction of the heat flow occurs, because the sample material is held by its surface tension. The effects of the maximum depression of the sample (X' = m = 0) were estimated by numerical calculations and shown in Table 1.

Flatness of the copper surface: In the calculation of Fig. 2, the second layer copper plate was treated as a completely flat plate. But, the copper plate was machined by a lathe, and there may have been a slight taper from the center to the edge. The effects were estimated, putting the thicknesses of the copper plate at the center and the edge as X' and X, respectively.

In the right end columns of Table 1, the estimated errors due to the factors 1 - 10 are given, calculated by the method mentioned above. Concerning the error due to the temperature measurement, which is not given in Table 1, \( \Delta T \) is estimated at \( \pm 0.01^\circ \text{C} \), even if the measured temperature of the second copper layer always contains an error \( \pm 0.015^\circ \text{C} \), which corresponds to the minimum resolution of the temperature measuring instrument. Concerning the radiation heat transfer between the copper plates, precise error estimation is not so easy, because the absorption coefficient of the sample material is unknown. But the maximum error, \( \Delta T \), is estimated at 0.9% for the maximum temperature difference between the plates, assuming the sample material is transparent and the plates are nickel plated. Even if the temperature measurement errors of the heater plate and the fourth plate are comparable to that of the second plate, the effects on \( \Delta T \) are negligible. By the way, each sheath thermocouple in the copper plates was carefully calibrated in advance of the measurement. Moreover, the errors due to the numerical calculation, the time measurement, the temperature distribution at the heater plate and the conduction by the spacers are negligible. As a result, the meniscus causes the largest error among the error factors discussed above. In the experimental result of Fig. 9, therefore, the meniscus effects were modified by the above-mentioned method based on the photographs in Fig. 14. If all the above errors were added up, the total error would amount to \( +13.8 \pm 12.4 \), but actually, the errors cancel each other and the total error is considered to be below \( \pm 5\% \). As is clear from Table 1, the accuracy of the measurement will be improved considerably, if the sample heat capacity is known accurately.

6. Conclusions

A transient measuring method of the thermal diffusivities of molten salts was proposed. In the method, the surface of the semi-infinite sample is heated with an arbitrary time function, and the thermal diffusivity of the sample is determined from the temperature responses at the heater and two points within the sample, using the numerical calculation. The accuracy of the temperature measuring point locations is improved by inserting copper plates within the sample. The heat loss through the sample container is minimised by holding the liquid sample between the copper plates by its own surface tension.

The measured thermal diffusivities for pure water, lithium nitrate and sodium nitrate agree with the results obtained by other authors. Concerning the result for sodium nitrate, which is considerably scattered depending on the authors, the accuracy of the result was estimated, discussing various possible error factors and their effects on the measured thermal diffusivity.

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